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Calculation of spin-densities within the context of density functional theory. The crucial role of the correlation functional

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It is demonstrated that the LYP correlation functional is not suited to be used for the calculation of electron spin resonance hyperfine structure (HFS) constants, nuclear magnetic resonance spin-spin coupling constants, magnetic, shieldings and other properties that require a balanced account of opposite- and equal-spin correlation, especially in the core region. In the case of the HFS constants of alkali atoms, LYP exaggerates opposite-spin correlation effects thus invoking too strong in-out correlation effects, an exaggerated spin-polarization pattern in the core shells of the atoms, and, consequently, too large HFS constants. Any correlation functional that provides a balanced account of opposite- and equal-spin correlation leads to improved HFS constants, which is proven by comparing results obtained with the LYP and the PW91 correlation functional. It is suggested that specific response properties are calculated with the PW91 rather than the LYP correlation functional. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2047467]

I. INTRODUCTION

Density functional theory (DFT)[1,2] is the most used quantum chemical tool for describing the properties of atoms and molecules.[3–6] Despite its many advantages it suffers from the fact that the exact density functional is not known and a systematic improvement of approximate functionals is rather difficult. Often improvements of density functionals can only be achieved by reverting back to the repertoire of wave function theory (WFT) and trying to combine features of WFT and DFT.[7–12]

A necessary requirement for improving standard Kohn–Sham (KS) DFT is the basic understanding of the electronic effects accounted for by the approximate exchange-correlation (XC) functionals in use today. In recent work, we have made several steps in this direction by describing exchange and correlation effects included by a given XC functional with the help of suitable difference densities,[13–16] by analyzing the effect of the self-interaction error of X functionals via the X-hole[17–19] or separating intrinsic and external nondynamic correlation effects in BS-UDFT or other two-configurational DFT approaches.[20,21]

In this work, we focus on the observations that atomic and molecular energies as well as molecular geometries and vibrational frequencies are reasonably described by the generalized gradient approximation (GGA)/XC functional BLYP (Refs. 22 and 23) or the hybrid XC functional B3LYP (Ref. 24) (actually optimized for this purpose) whereas magnetic properties such as magnetic shieldings [nuclear magnetic resonance (NMR) chemical shifts] or NMR spin-spin coupling constants (SSCCs) are sometimes better described by the GGA functional BPW91 (Refs. 22 and 25) or the hybrid XC functional B3PW91,[24(a)] sometimes not. These facts are documented in many research papers[26,27] and one way to approach the question of the performance of BLYP versus BPW91 (B3LYP versus B3PW91) would be to identify the electronic features of the molecules investigated and to relate them to known properties of the XC functionals under consideration.

The performance of any XC functional is best assessed by (a) separating exchange and correlation description[13–16] and (b) investigating simple electronic systems for which the correlation effects can easily be identified and analyzed. For example, if one considers just atoms rather than molecules, then of the three basic electron pair correlation effects (left-right, angular, and in-out correlation) just in-out correlation remains. The analysis will be further simplified if a property is investigated that is sensitive to exchange and correlation effects in a well understood way. Such a property is the hyperfine structure (HFS) constant of electron spin resonance (ESR), which is straightforwardly connected to the electron spin density.[28–32] For many atoms, reliable experimental values of the HFS constants are available. Alkali atoms[33,34] represent perhaps the simplest example, where the values of the hyperfine constants are directly related to the *ns* electron and its interaction with the core electrons.

The analysis of the HFS constants can be related to the *ab initio* and DFT description of other magnetic properties. For example, the Fermi contact term of the indirect nuclear SSCC in NMR spectroscopy is closely related to the Fermi contact term of the HFS constant.[35] Both require a correct description of the density at and close to the nucleus, which leads to similar requirements for the XC functionals of DFT.

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For the magnetic shielding (chemical shifts) of NMR spectroscopy the paramagnetic term is most difficult to describe.[36] We will see that the observations made for HFS constants and SSCCs can be directly related to the paramagnetic part of NMR magnetic shieldings or other response properties.

Clearly, it is desirable to investigate the full group of alkali elements from Li to Fr because one can expect that the differences to be discovered become especially strong for Rb, Cs, or Fr. Hence, it is appropriate to describe all atoms at a comparable and reliable level of theory. This requirement implies the use of (a) a relativistic treatment at all levels of theory considered, (b) the introduction of a highly correlated *ab initio* method (best coupled cluster or similar) for reference purposes both with regard to exchange (exact) and correlation (nearly exact), and (c) the use of response densities for analysis purposes to relate HFS constants directly to changes in total and spin densities. For the relativistic treatment, we will utilize the IORAmm method[37,38] based on the regular approximation[39] to the exact relativistic Hamiltonian developed recently by us. We have shown that a reliable description of magnetic effects in atoms and molecules can be obtained with this method when it is combined with a density functional or an *ab initio* wavefunction approach.[40,41]

We will proceed in this work in the following way. In Sec. II, we will describe the methods used in this study in more detail. Calculated HFS constants will be presented in Sec. III, and, for cesium atom as an appropriate example, we will analyze the HFS constants obtained with *ab initio* and various DFT XC functionals utilizing the response densities obtained at the same level of theory. We will show that the inferior performance of an otherwise perfectly performing hybrid functional such as B3LYP is a direct consequence of the fact that the correlation functional LYP (Ref. 23) was designed to describe correlation in the two-electron system He correctly[7] and therefore lacks important correlation effects of multi-electron systems, which are needed for the adequate description of magnetic properties.

II. FORMALISM AND DETAILS OF CALCULATIONS

In the present paper, we report the results of the calculations of isotropic HFS constants for the series of alkali atoms Li through Fr. The calculations are carried out at the nonrelativistic as well as at the quasirelativistic level of theory, which employs the infinite order regular approximation with the modified metric (IORAmm) method.[37] Within the context of DFT, several widely used XC functionals were employed: the GGA functionals BLYP (Refs. 22 and 23) and BPW91,[22,25] and the hybrid functionals B3LYP and B3PW91.[24] For comparison, wavefunction calculations at the Hartree–Fock (HF) and the correlation corrected QCISD (coupled cluster theory in the Quadratic Configuration Interaction approximation with all Single and Double excitations) level[42] were carried out. In the latter case, core and valence electrons were correlated. All calculations were performed with the help of the COLOGNE2005 suite of quantum-chemical programs,[43] which contains the IORA/IORAmm formalism for the calculation of HFS constants.[41]

The spin-unrestricted formalism was used throughout this work. Within this formalism, the isotropic HFS constant A_{iso}^{N} for the magnetic nucleus N is calculated according to Eq. (1):[30a,41]

$$A_{\mathrm{iso}}^{N} = -g_e g_N \mu_B \mu_N \langle S_z \rangle^{-1} \mathrm{tr}(\mathbf{H}_{\mathrm{FC},z}^{N} \mathbf{D}), \tag{1}$$

where g_e, g_N, μ_B, and μ_N are the electron and nuclear g-factors, and the Bohr and nuclear magnetons, respectively. $\langle S_z \rangle$ is the expectation value of the z component of the electron spin operator $\hat{\mathbf{S}}$, $\mathbf{D}$ the one-particle density matrix expanded in terms of basis set functions, and $\mathbf{H}_{\mathrm{FC},z}^{N}$ the matrix of the z component of the Fermi coupling operator $\hat{\mathbf{h}}_{\mathrm{FC}}$.

The nonrelativistic Fermi coupling operator is given in Eq. (2):

$$\hat{\mathbf{h}}_{\mathrm{FC}}(\mathbf{r}_N) = \frac{8\pi}{3} \delta(\mathbf{r}_N) \hat{\mathbf{S}}, \tag{2}$$

where $\delta(\mathbf{r})$ is the Dirac delta function and $\mathbf{r}_N$ the electron position with respect to the magnetic nucleus N. Note that Eq. (1) is applicable within the self-consistent field spin-unrestricted HF and KS formalisms as well as within any correlated wavefunction formalism provided that the so-called relaxed density matrix (i.e., the density matrix which incorporates the first order response)[30a,44] is used.

The appearance of the Dirac delta-function in Eq. (2) means that, within the nonrelativistic formalism, the isotropic HFS constants probe the spin density at the atomic nucleus. The relativistic expression for the Fermi coupling operator $\hat{\mathbf{H}}_{\mathrm{FC},z}^{N,\mathrm{rel}}$, which was presented in our earlier publications[40,41] and is not reproduced here for the sake of brevity, is straightforwardly related to the $\mathbf{H}_{\mathrm{FC},z}^{N}$ in Eq. (2). The relativistic operator is, however, nonlocal and probes the spin density in the vicinity of the nucleus and not just at the nuclear position.

The basis sets employed in this work are taken from our previous work on the hyperfine structure constants.[41] That is, a [16s3p2d1f] set for Li derived from the Dunning's aug-cc-pVTZ basis set,[45] a [18s5p2d] set for Na, a [20s7p2d] set for K, a [22s9p4d] set for Rb, a [24s11p6d] set for Cs, and a [16s12p8d2f] set for Fr derived from the aug-cc-pVTZ basis sets of Sadlej.[46]

III. RESULTS AND DISCUSSION

The results of density functional and *ab initio* wavefunction calculations of the isotropic HFS constants of alkali metal atoms Li through Fr are collected in Table I alongside with the experimental data. For each entry, the upper line contains the results of the quasirelativistic IORAmm calculations whereas the nonrelativistic results are given in the lower line. The importance of the relativistic contraction of the atomic s orbitals for the HFS constants is apparent from comparison of the IORAmm and nonrelativistic results from Table I. The IORAmm/QCISD results in Table I compare fairly well with the experimental values and, therefore, they are used as reference data for other calculated HFS constants.

The dynamic electron correlation accounted for by QCISD makes a sizable contribution to the HFS constants as

TABLE I. Hyperfine splitting constants (in MHz) of alkali atoms.[a]

Method	^{7}Li	^{23}Na	^{39}K	^{87}Rb	^{133}Cs	^{211}Fr
Exptl. [b,c]	401.752	885.816	230.860	3417.342	2298.158	8692.2
QCISD	401.643	866.984	226.127	3455.291	2409.961	8436.7
	401.058	849.331	211.871	2696.144	1426.990	2945.5
SCF	390.673	781.566	189.727	2926.352	2052.398	7733.7
	390.099	765.572	177.600	2268.093	1186.676	2441.6
BLYP	460.946	1018.917	254.957	3948.954	2729.283	8922.1
	462.254	999.908	239.364	3102.047	1647.263	3430.4
BPW91	384.483	904.489	227.623	3678.544	2570.683	8833.1
	384.420	886.945	213.401	2860.423	1516.058	3187.2
B3LYP	454.420	995.320	250.871	3899.739	2719.439	9143.9
	455.337	976.289	235.367	3055.266	1628.003	3390.4
BH&HLYP	464.749	965.089	242.491	3753.148	2634.811	9180.9
	465.738	946.390	227.359	2932.264	1561.273	3242.8
B3PW91	391.249	898.690	227.408	3648.440	2566.664	8993.7
	391.038	880.973	213.114	2834.977	1508.338	3162.4

[a]See text for details on the basis sets employed in the calculations. For each quantum-chemical method, the first line contains values obtained with the IORAmm relativistic method, whereas the second line gives the nonrelativistic values.
[b]Values for Li to Cs taken from Ref. 32.
[c]Value for Fr taken from Ref. 33.

is revealed by a comparison of QCISD and HF results in Table I. The inclusion of correlation has two opposing effects, namely one in the core region leading to density contraction and one in the valence region leading to density expansion. In the inner core region, a correlated motion of the electrons improves screening of the repulsive interaction between the two opposite-spin electrons and a better packing of electrons around the nucleus, i.e., in the 1s shell density is contracted toward the nucleus upon inclusion of dynamic correlation. This is reflected by an increase in the HFS constant. Note, that the nonrelativistic isotropic constant depends on the electron spin density at the nucleus only, whereas the relativistic constant is nonlocal and depends also on the spin density in the vicinity of the nucleus. This leads to a somewhat larger correlation increment for the relativistic HFS constant than the nonrelativistic one.

A direct and an indirect effect of dynamic correlation is observed for the valence density. The mixing of unbound one-electron states (orbitals) into the wavefunction leads to more diffuse bound one-electron states (orbitals) and to an expansion of the density. This effect is increased by the fact that a stronger screening of the nucleus by the core density reduces the effective nuclear charge for the valence electrons.

The density variation due to electron correlation is illustrated in Fig. 1, which shows the radial density and radial spin density obtained by IORAmm/QCISD calculations of the cesium atom [Figs. 1(a) and 1(c)] along with the correlation contributions to these properties [Figs. 1(b) and 1(d)]. The radial density is defined as $\rho(\mathbf{r})=4\pi r^2 n(\mathbf{r})$, where $n(\mathbf{r})$ is the number density (the number of electrons per unit volume), and the radial spin density is defined similarly using the spin density $n_s(\mathbf{r})=n_\alpha(\mathbf{r})-n_\beta(\mathbf{r})$. Note that the use of the number density $n(\mathbf{r})$ instead of the radial density $\rho(\mathbf{r})$ may obscure observation of the effect of electron correlation, because the former density is strongly dominated by density peak at the nucleus and possesses less pronounced shell structure.

The radial density as well as the radial spin-density show a shell structure where the 1s, 2s2p, 3s3p, and 4s4p3d shells of cesium can be clearly identified. The outer shells are outside the region displayed in Fig. 1. As is evidenced by the difference radial density $\rho^{\mathrm{QCISD}}(\mathbf{r})-\rho^{\mathrm{HF}}(\mathbf{r})$, there is a depletion of density in the 2s2p, 3s3p, and 3d4s4p shells whereas the region between the latter two shells experiences an increase in density. The increase of density in the 1s shell as a result of correlation does not become visible because of the factor of $4\pi r^2$. However, the magnitude of the spin density $n_s(\mathbf{r})$ at the nucleus can be assessed from the values of the nonrelativistic HFS constants reported in Table I [Eq. (2)].

The spin density [see Figs. 1(c) and 1(d)] increases in the core shells upon inclusion of dynamic electron correlation at the QCISD level. Generally, the spin density can be decomposed into direct and spin-polarization contributions. The direct contribution is the density of the electron in the singly occupied atomic (or molecular) orbital. In the case of the cesium atom, the singly occupied atomic orbital obtained in the IORAmm/ROHF calculation contributes 1702.9 MHz to the isotropic HFS constant. The unpaired electron polarizes the electron pairs in the doubly occupied orbitals thus leading to a spin-polarization contribution to the total spin density, which increases the HFS constant to the value of 2409.9 MHz as reported in Table I. Hence, spin-polarization accounts for more than 25% of the total HFS constant.

The spin-polarization of the core electrons is primarily caused by the mixing of the virtual (unbound) one-electron states with the core electron states as mediated by the unpaired electron.[32] This is an exchange effect (only the same-spin electrons are involved) and it must therefore be described by the spin-unrestricted Hartree–Fock (UHF) approach.[47] The limited variational freedom of UHF due to

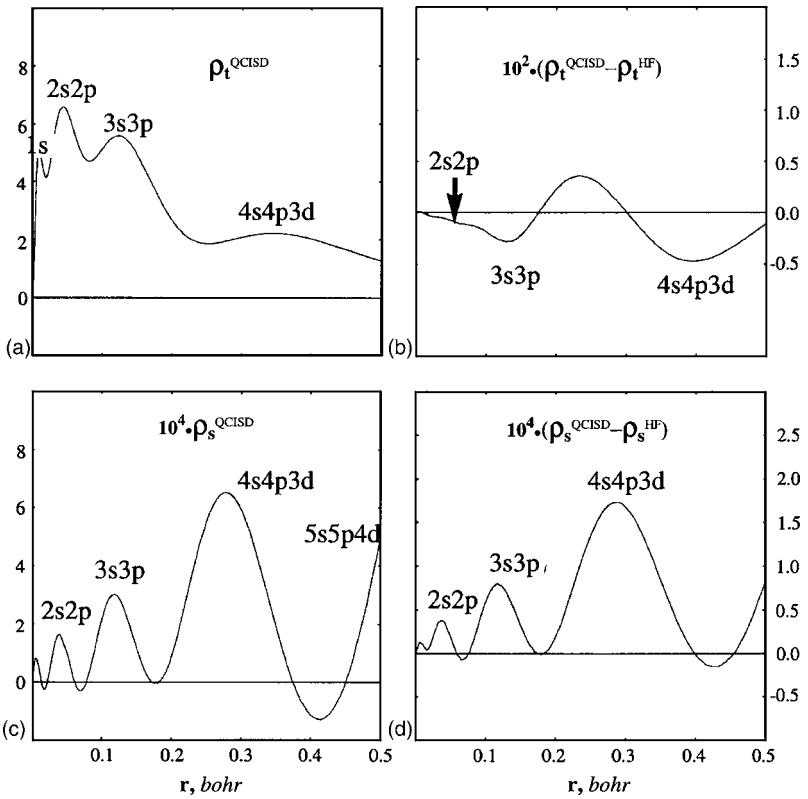

FIG. 1. Radial total density distribution ρ_t calculated at the QCISD level (a), difference radial total density distribution $\rho_t^{QCISD}-\rho_t^{HF}$ where ρ_t^{HF} is the HF reference density (b), radial spin-density distribution ρ_s calculated at the QCISD level (c), and difference radial spin density distribution $\rho_s^{QCISD}-\rho_s^{HF}$ (d) calculated for the cesium atom in its ^2S ground state using IORAmm/UHF and IORAmm/UHF-QCISD theory. Densities in $e \times bohr^{-3}$, radial distance in bohr. The shell structure of the cesium atom is visualized by associating maxima in ρ_t and ρ_s with specific shells and using the corresponding r values for the difference densities.

the use of a single determinant wavefunction leads to the coupling of exchange core polarization with an unspecified amount of in-out correlation effects for the atomic core electrons (reflected by the different spatial parts of α and β orbitals).[47] In-out correlation occurs between electrons of opposite spin located in the same electron shell and is therefore a strong effect, which affects the overall spin-density significantly. Although UHF accounts for some (a small part) of the in-out correlation, it cannot come close to providing a reasonable correlation correction.

The explicit account of electron correlation at the QCISD level leads to a noticeable increase in the spin density [see Fig. 1(d)], which amounts to up to 30% of the total spin density. Being predominantly caused by orbital orthogonality and exchange interactions, the direct (orbital) spin density and the exchange core polarization are not affected by the explicit inclusion of electron correlation. Consequently, the incomplete treatment of in-out correlation at the UHF level[47] leads to a noticeable negative contribution to the spin density of the atomic core (relative to the QCISD spin density).

Let us now turn to the DFT results. Inspection of the data in Table I reveals that, contrary to BPW91, the BLYP density functional overestimates substantially the nonrelativistic as well as the relativistic values of the atomic HFS constants, the latter by 10–15 %. The hybrid HF/DFT functionals show only marginal improvement over their pure DFT counterparts. Similar to the case of pure density functionals, B3PW91 yields markedly better results than B3LYP and BH&HLYP. Since the exchange functional used in these calculations is the same, the difference in the calculated HFS values is obviously caused by the correlation functional. Apparently, the PW91 gradient-corrected correlation functional is capable of producing more accurate results than the widely used LYP correlation functional.

In Fig. 2, the radial densities $\rho(\mathbf{r})=4\pi r^2 n(\mathbf{r})$ obtained from DFT calculations for cesium are compared with the corresponding densities from QCISD. The BLYP and BPW91 total radial densities do not show any apparent differences. They are both characterized by a certain density depression inside the atomic shells accompanied by an increase in the intershell regions [Figs. 2(a) and 2(b)]. This smoothening of the atomic shell structure is the result of insufficiently pronounced intershell barriers in the exchange-correlation potential generated by a gradient-corrected functional as was demonstrated by van Leeuwen and Baerends.[48] In the immediate vicinity of the nucleus, there is an upsurge of the DFT density relative to that of the QCISD density. This density hike, which is obscured by the factor $4\pi r^2$ in the radial density, is due to the well-known divergence of the exchange-correlation potential generated by a gradient-corrected functional.[49] Besides a typical distortion of the atomic shell structure, the total density produced by the two XC functionals suggests an exaggeration of electron correlation effects in the total density [Figs. 2(a) and 2(b)].

Whereas the total densities from the two DFT calculations do not suggest any significant differences, the radial spin densities shown in Figs. 2(c) and 2(d) are strikingly different. The BLYP functional produces a spin density, which deviates markedly from the reference QCISD spin density [Fig. 2(c)]. The spin-density accumulation within the atomic core shells [see Fig. 1(c)] is seriously exaggerated by the LYP correlation functional [Fig. 2(c)]. In contrast to LYP,

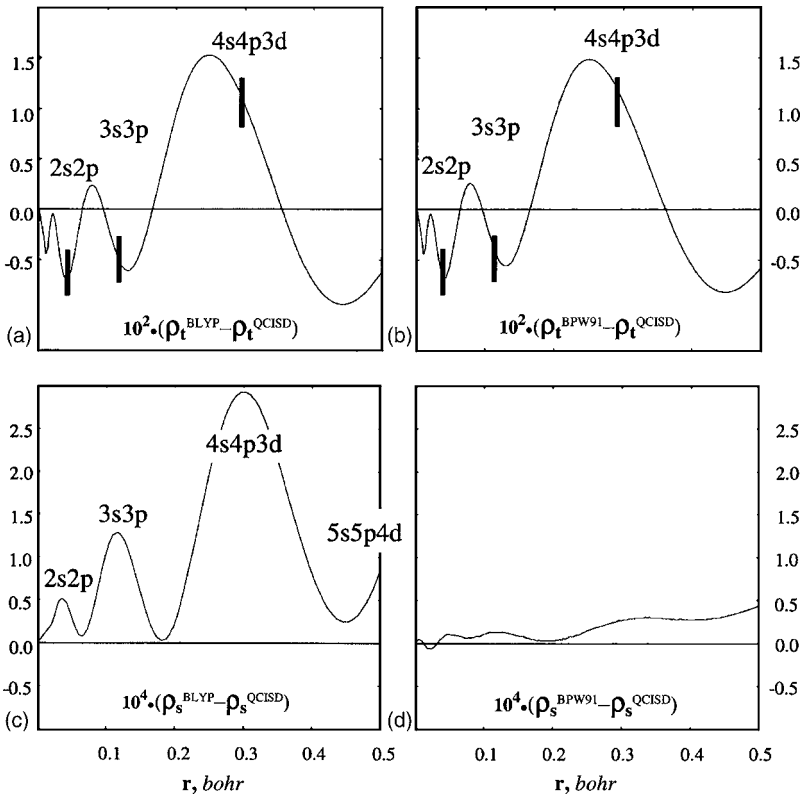

FIG. 2. Difference radial total density distribution $\rho_t^{\mathrm{BLYP}} - \rho_t^{\mathrm{QCISD}}$ (a), difference radial total density distribution $\rho_t^{\mathrm{BPW91}} - \rho_t^{\mathrm{QCISD}}$ (b), difference radial spin-density distribution $\rho_s^{\mathrm{BLYP}} - \rho_s^{\mathrm{QCISD}}$ (c), and difference radial spin density distribution $\rho_s^{\mathrm{BPW91}} - \rho_s^{\mathrm{QCISD}}$ (d) calculated for the cesium atom in its ^2S ground state using IORAmm/UDFT and IORAmm/UHF-QCISD theory. Densities in $\mathrm{e} \times \mathrm{bohr}^{-3}$, radial distance in bohr. The shell structure found in Fig. 1 for ρ_t and ρ_s is used by denoting its maxima by vertical lines [see (a) and (b)].

the PW91 correlation functional produces a spin density, which is remarkably close to that of the QCISD description [Fig. 2(d)].

In the spin-unrestricted mean field theory (UHF or UDFT), the overall spin density within the atomic core region results from a combination of three different factors: (a) the direct (orbital) contribution, (b) the contribution due to exchange core polarization, and (c) that due to in-out correlation.[32,47] The influence of the correlation functional on the direct contribution is minimal, because the shape of the singly occupied atomic orbital in the valence shell is strongly determined by the orthogonality to the inner atomic shells. The exchange core polarization is enforced by the exclusion principle and it also cannot be strongly affected by the correlation functional. Hence, it is the in-out correlation of the atomic core electrons, which is strongly influenced by the choice of the correlation functional.

As we have seen for the UHF method, in-out correlation makes a negative contribution to the total spin-density within the spin-unrestricted mean field approach. It follows from the spin-density diagrams in Fig. 2 that for the LYP correlation functional there is no longer a significant negative contribution (relative to QCISD). This results in an overestimation of the spin-polarization contribution to the spin density, which exceeds even the effect of the dynamic electron correlation accounted for in the QCISD method [see Fig. 2(c)].

The effect of in-out correlation on the wavefunction and, consequently, on the spin density, depends on the strength of the opposite-spin electron correlation accounted for by a correlation functional. The correlation functional affects the repulsion in the opposite spin electron pairs by making it weaker than in the case of an exchange only description. Therefore, the magnitude of the spin polarization attributed to in-out correlation decreases in absolute value (i.e., it becomes less negative than in a UHF description).

The HFS constants in Table I and the spin densities in Fig. 2 imply that LYP provides the strongest correlation between opposite-spin electrons. Indeed, this functional does not take into account the correlation between same-spin electrons at all, yielding zero correlation energy for a completely spin-polarized [i.e., $n(\mathbf{r}) = n_\alpha(\mathbf{r})$] many-electron system.[23] At the same time, the LYP correlation functional yields reasonable total correlation energies for atoms. This means that, according to the LYP description, the total correlation energy (resulting from opposite and equal spin correlation) is due to the opposite-spin correlation only. Consequently, LYP overestimates the opposite-spin correlation energy.

This statement can be illustrated by the numbers available from the literature.[50] For instance, the exact total correlation energy of the neon atom is 0.391 hartree and the correlation energy due to the opposite-spin electron pairs is 0.308 hartree. The PW91 functional yields 0.382 hartree for the total and 0.306 hartree for the opposite-spin correlation energy. The LYP functional yields 0.383 hartree for both, because there is no same-spin component of the correlation energy within LYP. Thus, LYP overestimates the opposite-spin component of the correlation energy by about 0.076 hartree.

The fact that it is the opposite-spin correlation energy that plays a decisive role for obtaining good spin densities explains why an admixture of exact (Hartree–Fock) exchange does not lead to a noticeable improvement. For instance, the BH&HLYP functional, which blends the HF and DFT exchange in equal proportion, produces the same poor spin densities as its "pure" counterpart BLYP. Even 100% of

HF exchange as present in the HF-LYP functional do not improve the spin density relative to the BLYP spin density. Crucial for obtaining reasonable spin densities in UDFT calculations is a balanced description of opposite-spin versus same-spin correlation effects.

IV. CONCLUSIONS

Our investigation of HFS constants calculated at the UDFT level of theory demonstrates that the LYP correlation functional is not suited for the determination of properties that require a balanced account of opposite- and equal-spin correlation. Clearly, this is the case for any property that depends on spin-density distribution, especially in the core region. Beside the HFS constants, this is also true for the SSCC because its Fermi contact (FC) term and spin dipole term are determined by the spin-density distribution. As a matter of fact, the HFS constant and the FC term of the isotropic indirect SSCC are closely related.[35] We predict that the BPW91 or B3PW91 functional is better suited for SSCC calculations than the BLYP or B3LYP functional.

In the case of the HFS constant, the spin polarization of the core electrons is a response of the core electrons to the presence of a single (unpaired) electron in the valence shell. Similarly, the paramagnetic contribution to the magnetic shielding constant is a response of the density, especially that close to the nucleus, on the influence of an external magnetic field. Therefore, magnetic shielding constants are also sensitive to a correct description of equal- and opposite-spin correlation, which is better provided by PW91 than LYP. Similar considerations hold for the paramagnetic spin orbit term of the SSCCs, the magnetizability (or its macroscopic analogue, the magnetic susceptibility) of a molecule, the electric field gradient at the nucleus, or the nuclear quadrupole shielding factors.

For calculated NMR chemical shifts (derived from magnetic shieldings by using a suitable reference shielding) it was shown that BPW91 performs better than BLYP or B3LYP.[26] Our work clarifies that the performance of any XC functional using C=LYP is hampered by the lack of equal spin correlation and the exaggeration of opposite-spin correlation.

Indeed, for calculating the paramagnetic contribution of the magnetic shielding one needs the perturbed wave function, which implies that the wave function is varied under the impact of the perturbation operator. In practice, this means the inclusion of all single excitations due to the action of the perturbation operator. Any single excitation leads to a substantial change in equal spin vs opposite spin correlation. In other words, the paramagnetic contribution (contrary to the diamagnetic contribution, which depends just on the zero-order wave function) becomes sensitive to a proper account of both types of correlation, especially on their ratio to each other. In this way many molecular response properties depend on the correct description of equal-spin and opposite-spin correlation effects.

In the case of the NMR SSCCs one has to consider that calculated values depend on (a) the choice of the appropriate basis set (correct description of the core region), b) the inclusion of long-range electron correlation to avoid singlet-triplet instabilities by using local exchange functionals,[14–18] (c) the correction for rotational-vibrational effects (especially important when the nuclei of light atoms participate in spin-spin coupling), and (d) the consideration of environmental effects (specific and nonspecific solvation, cluster formation, temperature, pressure, etc.). We note that the data material presently available is not sufficient to clearly identify the role of equal-spin and opposite-spin correlation and the balanced description of these effects by the correlation functional. Therefore, previous observations, e.g., that B3LYP performs better than BPW91 or B3PW91 in SSCC calculations,[27] are not necessarily in conflict with the results of this work.

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